Matthew Vanagel
UAF Dept. of Chemistry
mgvanagel@alaska.edu

Preparation and Characterization of Sterically Hindered Dipyridil Pyrazine Derivatives

ABSTRACT:

With the intention of ultimately making a transition metal-containing helicene, the di-N-oxide of 2,3-bis(3-methylpyridin-2-yl) pyrazine was produced from 2,3-lutidiene over a series of eight reactions. ^{1}HNMR of intermediate products confirmed the expected structures and showed that each was sufficiently purified.

INTRODUCTION:

- Helicenes are ortho-fused aromatic rings that adopt a helical conformation to avoid the overlapping of the terminal rings.
- Their inherent chirality and the possibility of enantiomeric resolution makes helicenes promising candidates for chiral catalysts and ligands for asymmetric synthesis.
- Their potential comes from their high stability and resistance to isomerization[1].
- Here, we look to explore the potential bidentate ligand properties properties of sterically hindered dipyridil pyrazine derivatives.

Sheme 1. Synthesis of di-N-oxide of 2,3-bis(3-methylpyridin-2-yl)pyrazine. Reagents and conditions: (i) m-CPBA, $CHCl_3$, 20°C, 24 h; (ii) acetic anhydride, reflux 24 h; (iii) K_2CO_3, MeOH, H_2O, 20°C, 24 h; (iv) oxalyl chloride, CH_2Cl_2, DMSO, Et_3N, -60°C; (v) NaCN, EtOH, H_2O, reflux 1.5 h; (vi) I_2, CH_2Cl_2, 20°C, 1.5 h; (vii) 1,2-Diaminoethane, EtOH, chloranil, xylene, reflux 20 h; (viii) m-CPBA, CH_2Cl_2, 20°C, 24 h

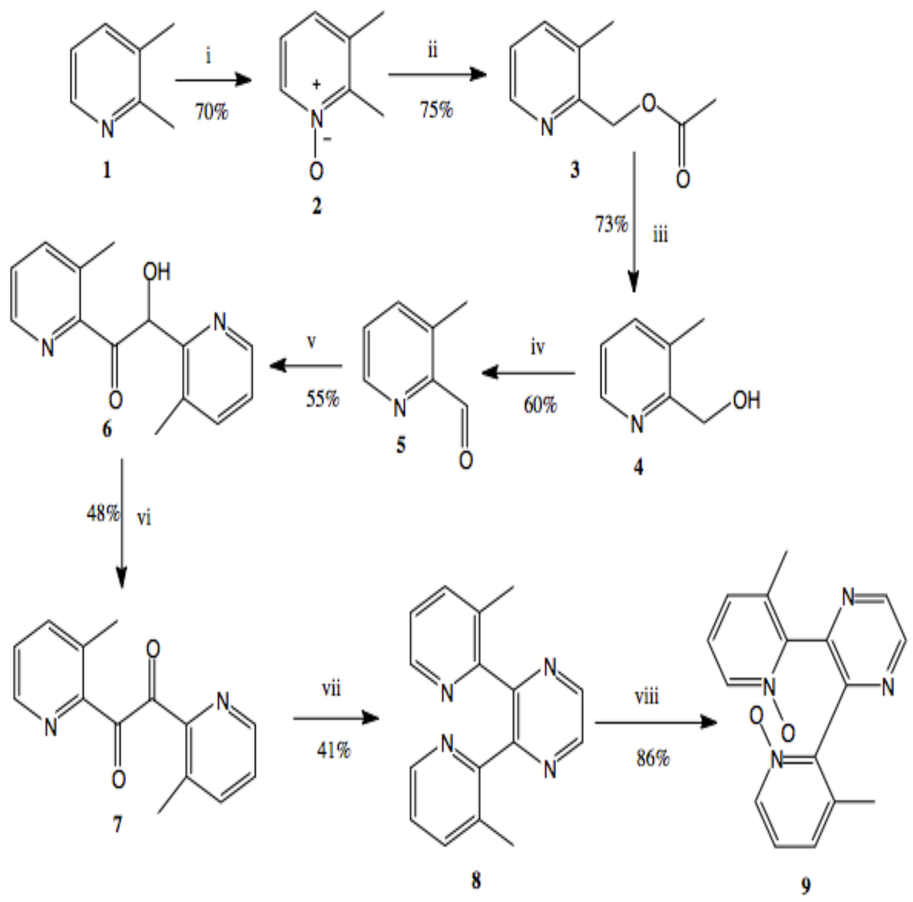
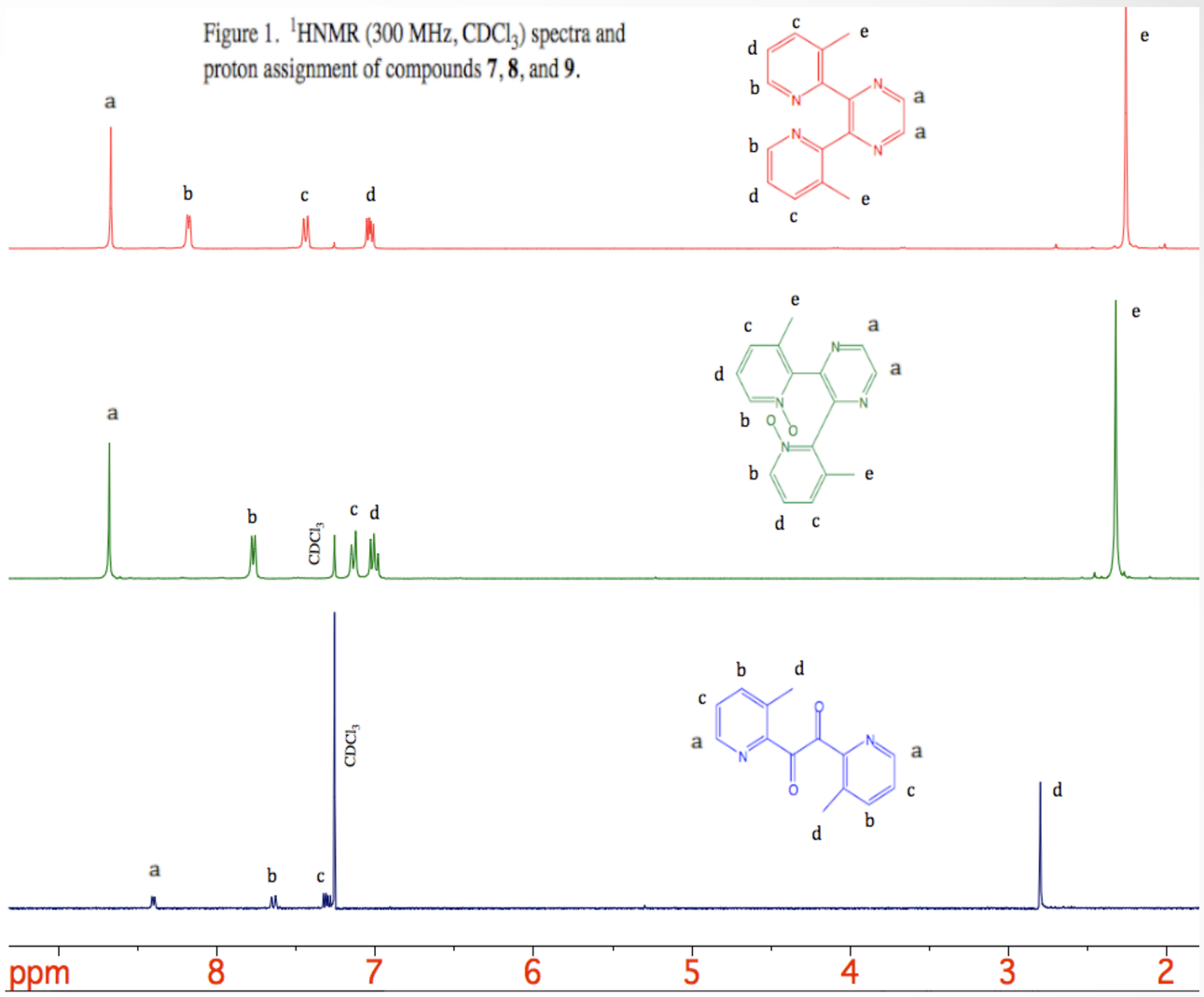


Figure 1. ^{1}HNMR (300 MHz, $CDCl_3$) spectra and proton assignment of compounds **7**, **8**, and **9**.



RESULTS & DISCUSSION:

Compound **2** was produced in a 70% yield based off of conditions adapted from *Kotar et al*[2]. Refluxing **2** with Ac_2O for 24 h afforded compound **3** in a 75% yield. Compound **4** was prepared from **3** and K_2CO_3 in a 73% yield. Compound **5** was produced by a Swern Oxidation in a 60% yield. Compound **6** was produced in a 55% yield from **5** and NaCN. I_2 and **6** afforded compound **7** in a 48% yield. Compound **8** was produced in a 41% yield from **7**, 1,2-diaminoethane, and chloranil in a procedure adapted from *Heirtzler et al*[3]. Finally, compound **8** was reacted with m-CPBA to afford **9** in an 86% yield.

Figure 1. shows ^{1}HNMR spectra of compounds **7**, **8**, and **9**. It is evident from the spectra that the compounds were sufficiently purified. Eventually a helicene compound will be prepared from **9** and its complexes with metal ions will be observed (**Figure 2**).

REFERENCES

1. Gingras, M. Chemical Society Reviews Volume 2 Issue 3. 2013 pg. 968-1006.
2. Kotar, Berta; Vrecer, Franc; Segula, Zakelj Mojca; Ritlop, Gregor. Novo Mestro. European Patenting Office. EP1681056A1. 19.07.2006
3. Heirtzler, Fenton; Neuburger, Markus; Zehnder, Margareta; Constable, Edwin C. Liebigs Ann. Recueil 1997, 297-301

Figure 2. Helicene molecule to eventually be synthesized